US005831209A

United States Patent [19]

Kozyrev et al.

[11] **Patent Number: 5,831,209**

[45] **Date of Patent: Nov. 3, 1998**

[54] **AEROSOL-FORMING COMPOSITION FOR THE PURPOSE OF EXTINGUISHING FIRES**

[75] Inventors: **Valeriy Nikolaevitch Kozyrev**, Moscow; **Valeriy Nilovitch Yemelyanov**; **Alexey Ivanovitch Sidorov**, both of Moskovskaya oblast'; **Vladimir Andreevitch Andreev**, Moscow, all of Russian Federation

[73] Assignee: **R-Amtech International, Inc.**, Bellevue, Wash.

[21] Appl. No.: **841,142**

[22] Filed: **Apr. 24, 1997**

[30] **Foreign Application Priority Data**

Apr. 30, 1996 [RU] Russian Federation 96108059

[51] **Int. Cl.**[6] **C06B 45/02**

[52] **U.S. Cl.** **149/21**; 149/19.1; 149/109.6; 252/5

[58] **Field of Search** 252/5; 149/21, 149/19.1, 109.6

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,608,641	9/1971	Cottrell	252/5
4,251,699	2/1981	Wiltgen	252/5
4,386,979	6/1983	Jackson	149/21
5,423,384	6/1995	Galbraith et al.	252/5
5,593,485	1/1997	Wang	252/2
5,610,359	3/1997	Spector et al.	149/19.6
5,613,562	3/1997	Galbraith et al.	149/61

FOREIGN PATENT DOCUMENTS

0561035A1	9/1993	European Pat. Off. .
2060743	4/1994	Russian Federation .
1764213	5/1988	U.S.S.R. .
1821985	10/1988	U.S.S.R. .
2020971	11/1979	United Kingdom .

Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—Rothwell, Figg, Ernst & Kurz, p.c.

[57] **ABSTRACT**

The present invention relates to a pyrotechnical, aerosol-forming composition for the purpose of extinguishing fires in confined spaces, containing potassium nitrate in a quantity of 67–72% by mass, phenolformaldehyde resin in a quantity of 8–12% by mass and dicyandiamide as the balance, wherein the particles of the potassium nitrate have a maximum average diameter of 25 μm, the particles of the phenolformaldehyde resin have a maximum average diameter of 100 μm and the particles of the dicyandiamide have a maximum average diameter of 15 μm,

A further object of the invention is a method for the preparation of the composition, which can be manufactured in conventional installations, by preparing a phenolformaldehyde solution using a mixture of ethyl alcohol with acetone in a ratio of 30–50:70–50 and by mixing and subsequently granulating during the drying process at 20°–70° C. The drying process is preferably performed at 40° C. by circulating air.

2 Claims, No Drawings

AEROSOL-FORMING COMPOSITION FOR THE PURPOSE OF EXTINGUISHING FIRES

FIELD OF THE INVENTION

The invention relates to fire-extinguishing technology, in particular the prevention and extinguishing of fires in confined spaces.

DESCRIPTION OF THE BACKGROUND ART

It is known, for the purpose of extinguishing a fire in a confined space, to create an atmosphere in this confined space which prevents combustion. As a fire-extinguishing agent inert thinning agents are used (carbon dioxide, nitrogen, argon, water vapour), volatile inhibitors, in particular halogen-containing agents, fire-extinguishing powders (A. N Baratov, E. M Ivanov, "Löschen von Bränden in der chemischen und erdölverarbeitenden lndustrie", Moskau, Chemie, 1979) ["Extinguishing fires in the chemical and petroleum processing industry", Moscow, Chemistry, 1979].

The known methods for the purpose of extinguishing fires in confined spaces using inert thinning agents cannot be used for extinguishing alkali and alkaline earth metals, some metal hydrides and compounds, which contain oxygen in their molecules.

In the development of systems for the purpose of extinguishing fires in confined spaces the possibilities are limited owing to the dimensions of the buildings which are to be protected (in the case of buildings with extremely large dimensions it is very difficult to be able to provide a sufficient quantity of gas in a given period of time). Furthermore the possibility of putting persons present in danger of suffocation must also be taken into consideration (therefore signal installations are necessary to indicate the deployment of the extinguishing procedure).

Extinguishing fires using halogen-containing compounds likewise has a series of disadvantages. These compositions can have a toxic effect on human beings, since, when a fire is being extinguished, the halogen-containing compounds form thermal decomposition products which have a large corrosive effect. Furthermore confined spaces which are particularly endangered by fire are normally protected by extremely large fire-extinguishing systems for extinguishing fires in confined spaces, wherein halogen hydrocarbons are used. Owing to the international standards for the protection of the ozone layer in accordance with the Montreal protocol (1987) the use of the fluoro-hydrocarbons must be halved by the year 1995 and completely eradicated by the year 2000, since these substances comprise a great potential for damaging ozone

Systems are known for the purpose of extinguishing fires in confined spaces, wherein halogen-containing hydrocarbons are used (for example GB-PS 2 020 971). A disadvantage of systems of this type is their harmful effect on the environment. Furthermore systems of this type comprise fairly large dimensions and a fairly large weight so that their efficiency is Impaired when extinguishing fires in transport media, e.g in aeroplanes.

A method is known for the purpose of preparing a fire-extinguishing agent, wherein when a charge of a pyrotechnical mass is burnt a mixture of solid particles and inert gases is formed (WO 92/17244). However, the high temperature of the combustive products results in increasing the average ambient temperature in the confined space, which produces a harmful effect on persons therein. Furthermore,

when burning pyrotechnical solid combustion fuels, gaseous products (CO, NH_3, H_2, CH_x, and NO_x), in addition to the primary aerosol products having an extinguishing effect, develop from the incomplete combustion of the organic components, which leads to the environment being polluted by these products.

SUMMARY OF THE INVENTION

The composition in accordance with the invention achieves the object of providing an ecologically safe composition for the purpose of extinguishing fires in confined spaces.

An object of the invention is a pyrotechnical, aerosol-forming composition for the purpose of extinguishing fires in confined spaces, containing potassium nitrate in a quantity of 67–72% by mass, phenolformaldehyde resin in a quantity of 8–12% by mass, and dicyandiamide as the balance, wherein the particles of the potassium nitrate comprise a maximum average particle diameter of 25 μm and accordingly comprise a minimum specific surface area of 1500 cm^2/g, and the maximum average particle diameter of the phenolformaldehyde resin is 100 μm and the maximum average particle diameter of the dicyandiamide is 15 μm.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferably the composition in accordance with the invention also contains potassium bicarbonate ($KHCO_3$), potassium benzoate ($C_7H_5O_2K$) or potassium hexacyanoferrate $K_3[(FeCN)_6]$ having a maximum average particle diameter of potassium-containing material of 15 μm and accordingly having a minimum specific particle surface area of 500 cm^2/g. The composition contains (in % by mass):

potassium nitrate	67–72
dicyandiamide	9–16
phenolformaldehyde resin	8–12
potassium benzoate, bicarbonate or hexacyanoferrate	4–12

The object described is also achieved by virtue of the method for the preparation of the composition in accordance with the invention, which method comprises providing a solution of phenolformaldehyde resin, mixing the constituents, sieving out, granulating and drying, wherein for the preparation of the solution of the phenolformaldehyde resin a mixture of ethyl alcohol with acetone in a ratio of 30–50:70–50 is used, the powder-form constituents are mixed with the solution of the phenolformaldehyde resin by adding the solution in at least two equal portions until all constituents are distributed in a uniform manner in the whole mass, i.e until a uniform and stable mass is obtained, the mixture is granulated simultaneously during drying at temperatures of 20°–70° C. until a residual content of moisture and volatile constituents of not more than 1% is present and the granulated composition is sufficiently fluid when used.

The ratio and the dispersity of the constituents and the method for the preparation of the composition guarantee a more rapid and more complete combustion of the composition and a larger quantity of fine-grain particles and inert gases (CO_2, N_2, and H_2O as vapour) in the aerosol, thus in turn guaranteeing that the composition extinguishes efficiently and thus producing during the extinguishing procedure a toxic level which is acceptable to human beings.

The use of fine-grain starting products of the powder-forming components (potassium nitrate, dicyandiamide,

potassium benzoate, potassium bicarbonate, potassium hexacyanoferrate) and the use of phenolformaldehyde resin as a lacquer solution in ethyl alcohol/acetone mixture and the use of the method in accordance with the invention for the preparation of the composition render it possible to obtain a final mixture having the necessary technological properties and properties for use, and to reduce the duration of the preparation process and the risk of the said preparation process (the necessity for dangerous operations such as the circulation of air is obviated).

The composition in accordance with the invention can be prepared in standard pyrotechnical installations.

In table 1 formulations of the composition in accordance with the invention are illustrated in comparison to a known composition and the most important parameters of these compositions are also listed. It is evident from table 1 that the composition in accordance with the invention surpasses the known composition in all parameters listed.

In table 2 formulations of the composition in accordance with the invention (No. 11, 14, 16, 17, 18 and 21) are illustrated in comparison to compositions, wherein the quantity and/or the dispersity of the constituents are outside the range in accordance with the invention. It is evident from table 2 that the composition in accordance with the invention comprises a reduced toxic effect. Moreover, for the purpose of extinguishing fires, a lower concentration of extinguishing agent is required. Furthermore the composition in accordance with the invention guarantees a larger quantity of fine-grain particles and inert gases in the aerosol.

TABLE 1

Components, properties of the mixture	Concentration of the components (% by mass) properties 1	2	3	4	5	6	Nearest Prior Art WO 92/17244
Potassium nitrate	70	70	70	70	70	70	70
Dicyandiamide	12	12	12	9	9	9	19
Iditol (Phenolformaldehyde resin)	—	—	—	—	—	—	11
Phenolformaldehyde resin as a lacquer (solid body)	11	11	11	11	11	11	—
Potassium bicarbonate	7	—	—	9	—	—	—
Potassium benzoate	—	7	—	—	9	—	—
Potassium hexacyanoferrate	—	—	7	—	—	9	—
Speed of fire(mm/s)	2.1	2.5	2.3	1.8	2.3	21	1.5
Specific pressure of the pressing process*	1200	1200	1200	1400	1400	1400	2000
Yield at disperse phase (Mol-%)	56	64	62	53	58	57	48
Fire-extinguishing concentration for Ethanol (g/m^3)	40	35	35	45	40	40	50
Concentration of toxic gases (Vol-%)							
CO_2	0	0	0	0	0	0	0.018
NH_3	0.085	0.080	0.078	0.070	0.065	0.062	0.144

*) for the purpose of attaining coupl. (Coupling) = 0.95 kgf/cm^2

TABLE 2

No.	Concentration of component, % by mass, (average particle diameter, μm) KNO_3	Phenolformaldehyde resin	Gas-Aerosol-former	Toxic effect* Dead, %	Paralysed, %	Fire-extinguishing concentration g/m^3	Level of discharge into the aerosol, %
1	60(~320)	15(~360)	25(~340)DCDA**	79	100	48	76
2	67(<25)	10(<100)	23(~340)DCDA	0	4.2	36	88
3	60(<25)	8(~360)	32(~340)DCDA	100	100	42	80
4	67(<25)	18(<100)	15(~340)DCDA	0	58.3	38	84
5	60(<25)	8(<100)	32(~340)DCDA	100	100	40	84
6	70(<25)	5(~360)	25(<15)DCDA	0	12.5	36	86
7	70(<25)	15(<100)	15(<15)DCDA	0	4.2	34	90
8	70(<25)	18(<100)	12(<15)DCDA	0	16.7	36	90
9	60(<25)	15(<100)	25(<15)DCDA	79	79.2	42	80
10	58(<25)	5.5(<100)	36.5(<15)DCDA	79	100	56	78
11	69(<25)	12(<100)	17(<15)DCDA	0	4.2	26	97
12	65.5(<25)	14(<100)	20.5(<15)DCDA	0	17.4	28	95
13	68(<25)	13(<100)	29(<15)DCDA	0	4.2	26	96
14	70(<25)	11(<100)	19(<15)DCDA	0	0	24	99.3
15	54(<25)	12(<100)	34(<15)DCDA	100	100	120	68
16	70(<25)	11(<100)	12%(<15)DCDA + 7%(<15)KB	0	0	27	97
17	70(<25)	10(<100)	10%(<15)DCDA+ 10%(<15)KBC	0	0	22	99
18	69(<25)	8(<100)	11%(<15)DCDA 12%(<15)KHCF	0	0	23	98

TABLE 2-continued

No.	Concentration of component, % by mass, (average particle diameter, μm) KNO_3	Phenolformaldehyde resin	Gas-Aerosol-former	Toxic effect* Dead, %	Paralysed, %	Fire-extinguishing concentration g/m^3	Level of discharge into the aerosol, %
19	75(<25)	10(<100)	15%(<15)DCDA	12.5	100	40	90
20	76(<25)	15(<100)	9%(<15)DCDA	14.7	100	44	85
21	72(<25)	10(<100)	18%(<15)DCDA	0	0	26	97

*) The results are obtained from experiments conducted on white mice, which were subjected for a period of 15 minutes to a concentration of 60 g/m^3 and were monitored thereafter for a period of 2 weeks.
**) DCDA-dicyandiamide KB-potassium benzoate KBC-potassium bicarbonate KHCF-potassium hexacyanoferrate

EXAMPLE 1

Extremely favourable results are obtained when using the composition in accordance with the invention and the method for the preparation thereof, if the following formulation (% by mass) is used:

potassium nitrate with a specific particle surface area of 2000 cm^2/g	70
dicyandiamide with an average particle size of 12 μm	12
phenolformaldehyde resin as 50% solution in a mixture of ethyl alcohol and acetone in the ratio of 50:50 (calculated as a solid body)	11
potassium benzoate with a particle surface area of 600 cm^2/g	7

The preground powder-form constituents (potassium nitrate, dicyandiamide, potassium benzoate) are poured into a mixer and mixed for 10 minutes. Then a phenolformaldehyde resin solution is added in three equal portions. The contents of the mixture are mixed for 5 minutes in each case after the addition of the corresponding portion of the phenolformaldehyde resin. The mixing is performed at a temperature of 40° C., with an opened cover. The mixture thus obtained is emptied from the mixer and passed through a sieve into a granulator whilst being continuously aerated with hot air at a temperature of 40° C. The predried granulate is laid in bands in layers 2–3 cm thick and is dried up to 1% for the purpose of removing any further moisture and volatile constituents. The total time spent mixing and granulating amounts to approximately 1 hour.

The mixture thus obtained can be dried still further in a pressed state, if the amount of moisture and volatile constituents exceeds 1%.

The pyrotechnical, aerosol-forming composition in accordance with the invention and the method for the preparation thereof render it possible to charge aerosol fire-extinguishing generators therewith and with the aid of said extinguishing generators to extinguish in an effective manner a fire of gaseous, liquid and solid combustible materials in stationary confined spaces, in transport media in rail and road traffic, on ocean-going and river ships, in aeroplanes, also including blow-by devices for example in aeroplane engines, and likewise to detect fires and to prevent the transition from a fire in specialist manufacturing installations to an explosion in the storage areas and in production plants which are endangered by fire and explosion.

We claim:

1. Pyrotechnical, aerosol-forming composition for the purpose of extinguishing fires in confined spaces, containing potassium nitrate particles in a quantity of 67–72% by mass, phenolformaldehyde resin particles in a quantity of 8–12% by mass, and dicyandiamide particles as the balance, wherein the particles of the potassium nitrate comprise a maximum average diameter of 25 μm, the particles of the phenolformaldehyde resin comprise a maximum average diameter of 100 μm and the particles of the dicyandiamide comprise a maximum average diameter of 15 μm.

2. Pyrotechnical, aerosol-forming composition according to claim **1**, wherein it also contains particles of potassium bicarbonate, potassium benzoate or potassium hexacyanoferrate in a quantity of 4–12% by mass having a maximum average particle diameter of 15 μm.

* * * * *